HIRANUMA APPLICATION DATA	Automatic Titrator	Data No.	L13	Oct.24. 2024
Lubricant petroleum products	**Acid number in Petroleum products**			

1. Abstract

The acid number of petroleum products are one of the important index for judging its quality.

Measurement of acid number is indicated by "milligrams of potassium hydroxide required to neutralize acidic components contained in 1 g of the sample".

The international standard methods for acid number are shown as bellow.

- ASTM D664 : Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration
- JIS K2501 : Petroleum products and lubricants - Determination of neutralization number
- ISO 6619 : Petroleum products and lubricants – Neutralization number – Potentiometric titration method

This data sheet presents a potentiometric titration method according to ASTM D 664 (Test Method A Petroleum products and lubricating oils dissolved in toluene and 2-propanol).

The potentiometric titration process is as follows:

1) Weigh sample exactly corresponding to acid number and dissolve it in a titration solvent.
2) Immerse glass electrode and reference electrode.
3) Start titration with alcoholic potassium hydroxide solution.

Inflection point is defined as the end point if it obtained sharply (potential change of 15 mV or more at 0.05 mL titrant addition). If it's not clear, the endpoint is the potential mV indicated by the pH 10 standard. This data sheet shows examples of acid number measurements for samples with well-defined and unclear inflection points.

2. Configuration of instruments and reagents

(1) Configuration of instruments

Main unit	:	Automatic Titrator	COM Series
Electrode	:	Glass electrode	GE-103B (For non-aqueous titration)
	:	Reference electrode	RE-201Z
		(Inner solution: 1-3 mol/L lithium chloride ethanol solution)	

* Instead of glass and reference electrodes, the following glass-reference combination electrodes can also be used.

: GR-513BZ (for non-aqueous titration, movable sleeve type)

(2) Reagents

Titrant : 0.1 mol/L potassium hydroxide in 2-propanol standard solution

Titration solvent : Mixture of 500 mL of Toluene, 495 mL of 2-Propanol and 5 mL of water

pH 10 buffer solution : Used to determine endpoint potentials when inflection points are not available.

3. Measurement procedure

(1) Determination of the end point mV

i) Put the stir bar in pH 10 buffer solution and immerse electrodes. Read the mV value after the 5 minutes and is taken as the endpoint mV.

(2) Measurement of Acid number

i) A sample is taken in a 200 mL tall beaker and weighed to the nearest 0.1 mg digit. The amount of sample taken is determined by the expected acid value.

ii) Add 125 mL of titration solvent and dissolve sample by stirrer.
The stirrer speed must be adjusted to avoid the scattering of contents or taking the air into the solution.

iii) Immerse the electrodes and titrate by alcoholic KOH titrant until the end point mV.
Also, perform the blank test with the same procedure of sample measurement.

4. Measurement conditions and results

Examples of titration conditions

Measurement of endpoint potentials

Cndt No.	1	
Method	pH Meas.	
AMP No.	1	
D. Unit	mV	
S. Timer	300	sec

Measurement of blank

Cndt No.	2							
Method	Auto/Set		ConstantNo.	2		Mode No.	41	
Buret No.	1		Size	0	g	Limit Time	60	sec
Amp No.	1		Blank	0	mL	Del K	0	
D. Unit	mV		Molarity	0	mol/L	Del Sens	0	mV
S- Timer	30	sec	Factor	0		Int Time	10	sec
C.P. mL	0	mL	K	0		Int Sens	10	mV
Direction	↑		L	0		Brt Speed	2	
T- Timer	0	sec				Pulse	20	
D.P. mL	0	mL	Unit	mL				
End Sens	300		Formula	D				
End Point	-204.3	mV	Digits	3				
Over mL	-254.3	mV						
Max.Vol.	2	mL						

Measurement of sample

Cndt No.	3							
Method	Auto/Set		ConstantNo.	3		Mode No.	42	
Buret No.	1		Size	0	g	Limit Time	60	sec
Amp No.	1		Blank	0.097	mL	Del K	2	
D. Unit	mV		Molarity	0.1	mol/L	Del Sens	0	mV
S-Timer	30	sec	Factor	0.987		Int Time	10	sec
C.P. mL	0	mL	K	56.1		Int Sens	10	mV
Direction	↑		L	0		Brt Speed	2	
T- Timer	0	sec				Pulse	40	
D.P. mL	0	mL	Unit	mg/g				
End Sens	300		Formula	(D-B)*K*F*M/S				
End Point	-204.3	mV	Digits	3				
Over mL	-254.3	mV						
Max.Vol.	20	mL						

Measurement results

Measurement of blank

Number of measurements	Size (g)	Titrant volume (mL)
1	—	0.097
2	—	0.096
	Avg.	**0.097**

Measurement of sample No.1 (Endpoint: Inflection)

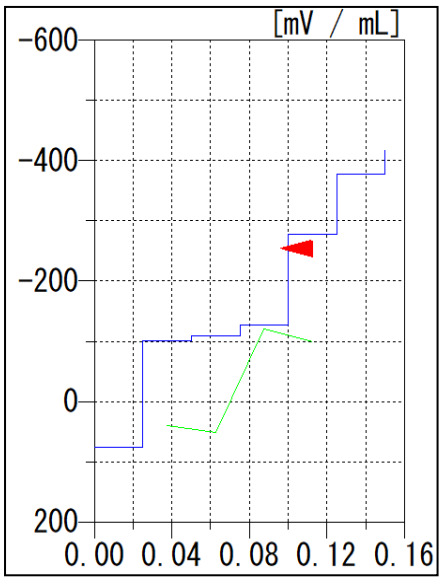
Number of measurements	Size (g)	Titrant volume (mL)	Acid number (mgKOH/g)
1	19.9892	2.963	0.794
2	20.0074	2.963	0.793
		Avg.	**0.794**
Difference between repetitive results		:	0.001
Repeatability limit		:	0.079

Reproducibility（Inflection）= 0.044(X+1)
X：The average of the two test results

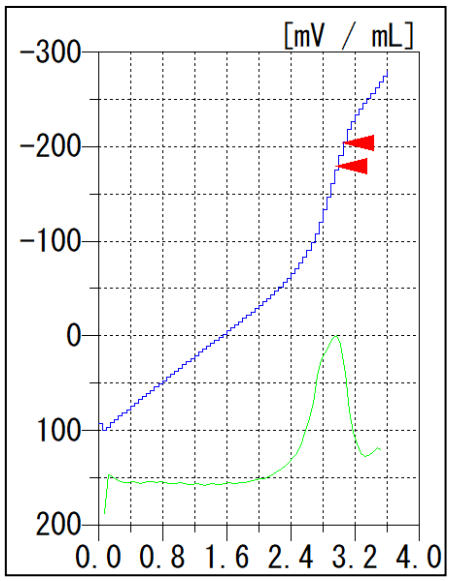
Measurement of sample No.2 (Endpoint: pH10)

Number of measurements	Size (g)	Titrant volume (mL)	Acid number (mgKOH/g)
1	0.9372	1.609	8.933
2	1.0030	1.726	8.993
		Avg.	**8.963**
Difference between repetitive results		:	0.060
Repeatability limit		:	1.049

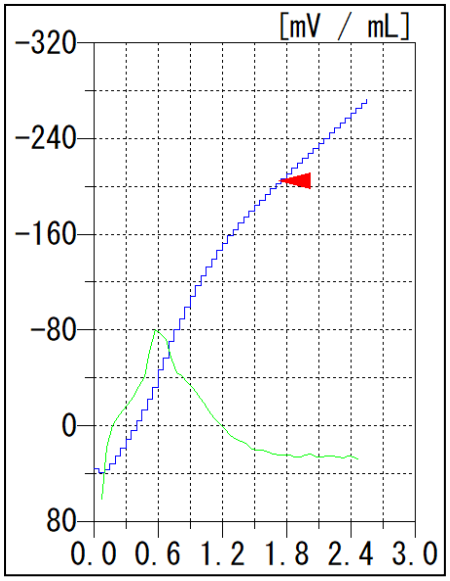
Reproducibility（Buffer EP）= 0.117X
X：The average of the two test results



Measurement of blank



Measurement of sample No.1



Measurement of sample No.2

Examples of titration curves

5. Note

(1) About endpoint detection

There are two methods for detecting endpoints.

1) To find the endpoint at the inflection point of the titration curve.

2) The endpoint is determined at a predetermined mV point on the titration curve.

Method 1) is applied to samples that show a clear inflection point on the titration curve. Method 2) is applicable to samples that do not show any inflection point on the titration curve.

(2) About titration control

According to ASTM D 664, the standard for stabilizing the potential at each drop is that if the potential changes by 10 mV or less in 10 seconds, the potential is considered to be stable and the next drop is added. The maximum waiting time for stability is 60 seconds. As an example of condition setting from the above, first, by setting the control mode No. to 41-50, the "Pre Int" is changed to "Limit Time" and set to 60 seconds. Also, set "Int Time" to 10 seconds and "Int Sens" to 10 mV.

The "Del K" is set to 0 for blank measurements, fixing each drop to the minimum titration volume. For sample measurement, it is set to "0" to "9", the higher the number, the larger the next titration volume. The minimum titration volume is 0.025 mL for blank measurement and 0.05 mL for sample measurement. When using a 20 mL syringe, set as shown in the example of titration conditions.

(3) Electrode

In this titration, a glass electrode (GE-103B) with a low-resistance glass membrane is used. This electrode has improved response due to its reduced internal resistance, and is expected to provide more stable results especially for non-aqueous neutralization titrations.

In addition, a movable sleeve type glass-reference combined electrode (GR-513B) can also be used in this titration instead of the glass electrode and reference electrode. Note that the internal solution must be

replaced with a 1-3 mol/L lithium chloride ethanol solution, and it is recommended to leave it to stand overnight after replacement.

It is recommended to activate the electrodes for about 5 minutes to pure water after each measurements. This is because when glass electrode is used for a long time in a nonaqueous solvent, the response speed and electromotive force decrease.

(4) Maintenance of buret

It is recommended to wash the flow channel of buret with water. This is because alcoholic KOH titrant have a tendency toward crystallization. When not using for a long time, please discharge titrant and then wash flow channel with water.

(5) 2-Propanol potassium hydroxide titrant

2-Propanol used as a solvent for the titrant has a relatively larger thermal expansion coefficient than water, and when the temperature changes by 1 °C, the titrant causes a volume change of 0.1 %. For accurate measurement, factor titration and sample measurement should be performed at the same room temperature as much as possible.

In addition, since this titrant is prone to change in factor due to absorption of carbon dioxide from the air, it is recommended to periodically standardize the titer with potassium hydrogen phthalate.

Keyword：ASTM D664, Petroleum products, Acid number, Potentiometric titration, Non-aqueous neutralization titration